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AFML-TR-68-130
Part I

SYNTHESIS OF POLYSPIROCYCLOBUTANES AND RELATED SPIROPOLYMERS
Part I.   Poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione)

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TECHNICAL REPORT AFML-TR-68-130, PART I

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SYNTHESIS OF POLYSPIROCYCLOBUTANES AND RELATED SPIROPOLYMERS
Part I. Poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione)

Clay M. Sharts
Derril L. Steele

FOREWORD

This report was prepared by San Diego State College Foundation, San Diego State College under USAF Contract No. F33615-67-C-1560, "Research on Synthesis of Polyspirocyclobutanes and Related Polymers." The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." The work was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg (MANP) as Project Scientist.

Work on this contract was performed by Dr. Clay M. Sharts, the principal investigator, and Mr. Derril L. Steele.

This report covers work conducted during the period of 1 March 1967 to 1 March 1968. It was submitted by the authors in April 1968.

This technical report has been reviewed and is approved.

W. E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

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ABSTRACT

Dispiro[3.1.3.1]decane-2,8-dicarboxylic acid was synthesized as a polymer intermediate from pentaerythritol via a seven-step process.

The diacid was converted to dispiro[3.1.3.1]decane-2,8-dicarbonyl dichloride and the bis-acid chloride dehydrohalogenated in benzene solution with triethylamine to give the corresponding diketene derivative. This unisolable monomer polymerized to poly(trispiro[3.1.3.1.3.1]-tridecane-1,3-dione).

An alternate procedure in place of the tedious synthesis of dispiro-[3.1.3.1]decane-2,8-dicarboxylic acid was investigated. In seeking a short route to the key intermediate, 1,1,3,3-tetrakis(hydroxymethyl)-cyclobutane, 3,3-bis(chloromethyl)oxetane was condensed with diethyl malonate to give diisoamyl and diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate. From these esters were formed diisoamyl and diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate. The hydroxyesters were polymerized to form a spiropolymer whose structure was probably that of poly[3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate].

Boron trifluoride-catalyzed polymerization of diethyl 6-oxaspiro-[3.3]heptane-2,2-dicarboxylate gave a polyoxetane.

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ILLUSTRATIONS

SECTION I

INTRODUCTION

The primary objective of this research is to synthesize polyspiro-cyclobutane type polymers. The initial direct objective is the synthesis of poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione), structure I.
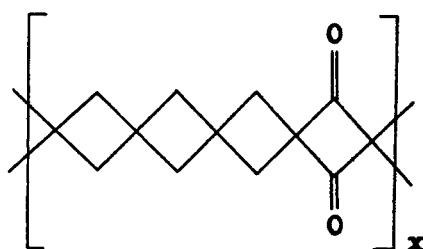
I

The second direct objective is to convert I into poly(1,1,3,3-tetra-fluorotrispiro[3.1.3.1.3.1]tridecane), structure II, and into poly(tri-spiro[3.1.3.1.3.1]tridecane), structure III. It is planned to convert I into II with sulfur tetrafluoride, and I into III by an appropriate Wolf-Kishner reduction or Raney-Nickel reduction of the appropriate thiol derivative.

II   III

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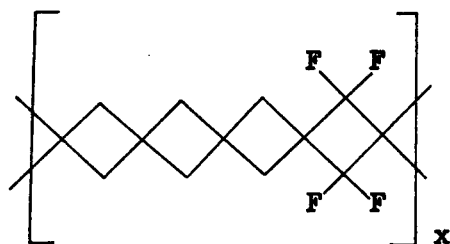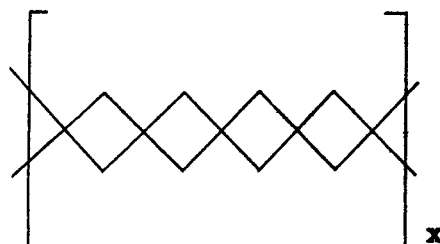
The synthesis of I was planned to be effected by dehydrochlorination of the bis-acid chloride (IV) derived from the known dispirodecane, [3.1.3.1]decane-2,8-dicarboxylic acid (Reference 1), to form an intermediate ketene which will polymerize to form I.
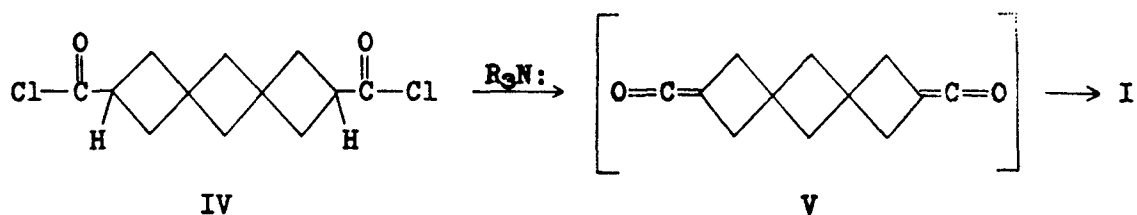
This polymerization reaction is based on a known synthesis by Buchman and Deutsch (Reference 2) in which they converted cyclobutanecarbonyl chloride into dispiro[3.1.3.1]decane-5,10-dione.

A secondary objective of this work is synthesis of related spiropolymers that appear feasible during the course of this work.

SECTION II

RESULTS AND DISCUSSION

A. Monomer Synthesis for Poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione)

The synthesis of dispirodecane[3.1.3.1]decane-2,8-dicarboxylic acid was accomplished by the previously reported synthesis (Reference 1). The steps in the synthesis are shown in Chart I and involved starting with pentaerythritol and proceeding stepwise through 2,2-bis (bromomethyl)propane-1,3-diol (VI), 2-phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane (VII), diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate (VIII), 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane (IX), 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane tetra-p-toluenesulfonate (X), and dispiro[3.1.3.1]-decane-2,2,8,8-tetracarboxylic acid (XI) to give, on decarboxylation, dispiro[3.1.3.1]decane-2,8-dicarboxylic acid (XII).

Prior to use in polymer synthesis compound XII was sublimed, crystallized twice from water and resublimed.

B. Poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione) - A Derivative of Polyspirocyclobutane

The most successful preparation of poly(trispiro[3.1.3.1.3.1]-tridecane-1,3-dione), compound I, was carried out in refluxing benzene solution. Diacid XII was treated with thionyl chloride to form diacid chloride IV. Excess thionyl chloride was removed under reduced pressure and dry nitrogen readmitted to the system. Dry benzene was distilled from sodium onto IV and a solution of IV in benzene formed. Dry triethylamine was codistilled with benzene from sodium into the benzene

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HOCH₂ / CH₂OH structures...

$HOCH_2$ — C — CH_2OH

$HOCH_2$ CH_2OH

$\longrightarrow$

$HOCH_2$ — C — CH_2Br

$HOCH_2$ CH_2Br

VI

O—CH_2 ... $COOC_5H_{11}$

C_6H_5-CH

O—CH_2 ... $COOC_5H_{11}$

VIII

$\longleftarrow$

O---CH_2 ... CH_2Br

C_6H_5-CH — C

O—CH_2 ... CH_2Br

VII

$HOCH_2$ ... CH_2OH

$HOCH_2$ ... CH_2OH

IX

$\longrightarrow$

$TsylOCH_2$ ... CH_2OTsyl

$TsylOCH_2$ ... CH_2OTsyl

X

$HOOC$ ... $COOH$

$HOOC$ ... $COOH$

XI

$\longleftarrow$

$HOOC$ — ... — $COOH$

XII
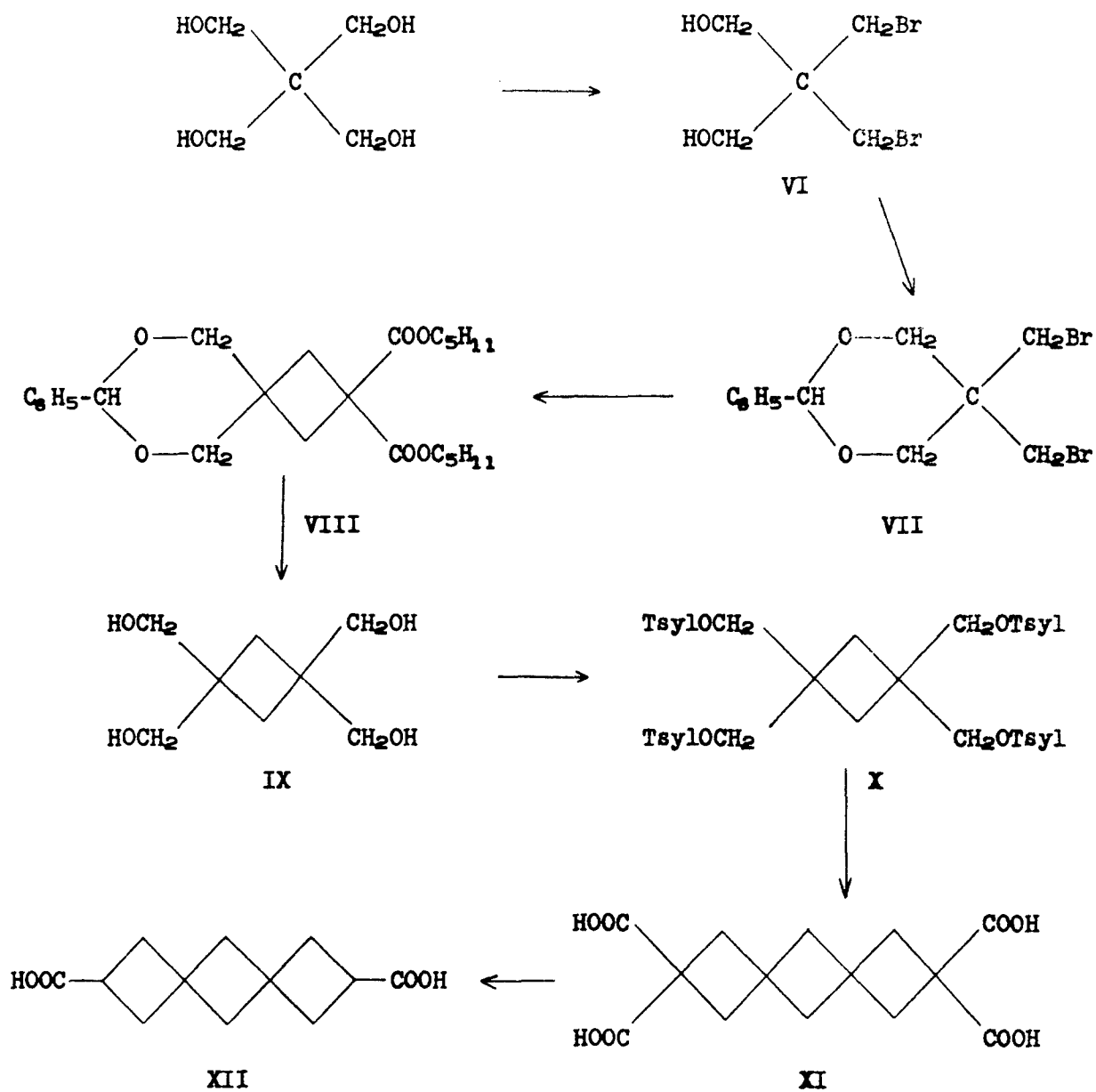
CHART I

Synthesis of Dispiro[3.1.3.1]decane-2,8-dicarboxylic Acid

solution of IV whereupon a white precipitate was observed to form in the reaction flask. The reaction mixture was stirred and heated for 24 hours under gentle reflux.

The white precipitate in the flask was filtered off and washed with hot water, boiled with hot water and isolated by filtration. The white solid was dried and the infrared spectrum recorded. Figure 1 is the infrared spectrum of this material, designated as High Grade Polymer I. On cooling, the benzene filtrate became a gel. Water was added and volatile material removed by steam distillation. The hot water mixture was filtered and insoluble white solid obtained. This solid was boiled again with water and separated by filtration. After drying the infrared spectrum of this material was obtained. Figure 2 is the infrared spectrum of this material, designated as Low Grade Polymer I.

Comparison of Figures 1 and 2 with Figure 3, the infrared spectrum of XII, will give an indication of the possible degree of polymerization of XII (or IV). In Figure 3, the carbonyl group of the diacid, XII, absorbs at 5.91 microns. Because of the method of work-up, it is presumed that polymer I has carboxylic acid end groups. Figure 1 has carbonyl absorption at 5.78 microns with a slight shoulder on the higher wavelength side. In contrast, in Figure 2 there is almost equal absorption at 5.78 and 5.91 microns. The infrared absorption of Figure 1 is interpreted as indicating that Low Grade Polymer I is probably no more than dimer and trimer. Monomer XII is absent because the method of work-up would be expected to extract hot-water-soluble XII from Polymer I. Characterization of Polymer I has not been carried out.

Other attempts to prepare Polymer I are summarized in Table I in the Experimental Section. From Table I it can be seen that higher temperatures appear to adversely affect polymerization. The alternative possibility is that tri-n-propylamine which was used in higher temperature

runs was not adequately purified. In some runs in benzene at reflux temperature, precipitated Polymer I became yellow at hot spots on the flask walls caused by the heating mantle. This suggests that excessive heat is the primary reason for adverse results at higher temperatures.

At present the degree of polymerization of Polymer I appears limited by solubility in benzene at the temperature of reflux. A solvent which keeps Polymer I in solution is desirable for the polymerization medium. Finding such a solvent will be difficult considering the highly reactive nature of the diketene intermediate, V, which leads to Polymer I.

C. Synthesis and Polymerization of Diethyl 6-Oxaspiro[3.3]heptane-2,2-dicarboxylate.

Since the synthesis of XII from pentaerythritol is tedious, a shorter synthesis was desired. In particular, an easier route to the key tetramethanol derivative, IX, was needed. The commercial availability from Hercules Chemical Company of Penton Monomer, 3,3-bis(chloromethyl)oxetane, suggested an alternate route. Synthesis of IX via diethyl 6-oxaspiro[3.3] heptane-2,2-dicarboxylate (XIII) was envisioned. Successful synthesis of XIII was accomplished by the route outlined below:
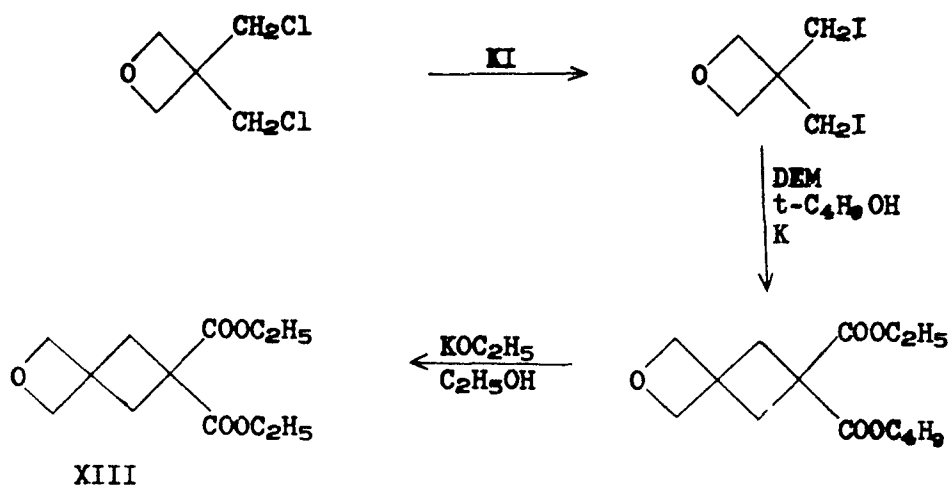
Penton Monomer® could not be condensed with diethyl malonate (DEM) under the normal conditions for malonate condensations. In diisoamyl alcohol condensation could be achieved; however, the product, diisoamyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate, could be separated from the monoalkylation side-reaction product only by an exceedingly careful distillation through a spinning-band column. 3,3-Bis(iodomethyl)-oxetane was easily prepared from Penton Monomer® by a published procedure (Reference 3). However, 3,3-bis(iodomethyl)oxetane did not condense with DEM in refluxing ethanol. Condensation was achieved in refluxing tert-butyl alcohol solution when potassium tert-butoxide was used as a base. The major product was the half-transesterified condensation product, ethyl tert-butyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate. Diethyl ester XIII was prepared by transesterification of the ethyl tert-butyl ester.

The initial justification for synthesis of XIII was to obtain a better source of 1,1,3,3-tetrakis(hydroxymethyl) cyclobutane (IX) which is considered the key intermediate for the synthesis of XII. The attempted reduction of diisoamyl 6-oxaspiro[3.3]heptane 2,2-dicarboxylate (XIIIa) with lithium aluminum hydride gave a difficultly separable mixture of IX and the oxetane-ring-opened product. Difficulty of the separation resulted in temporary abandonment of this route.
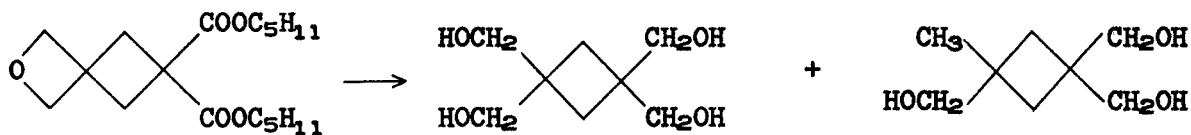
An attempt to open the oxetane ring of XIIIa first and then to reduce the ester groups was never carried past the ring-opening stage. Attempts to purify diisoamyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (XIVa) gave instead a polymer formed by transesterification

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and assigned the structure XV. Alternative structures to XV can be written; for convenience XV will be used until the structure is otherwise established.
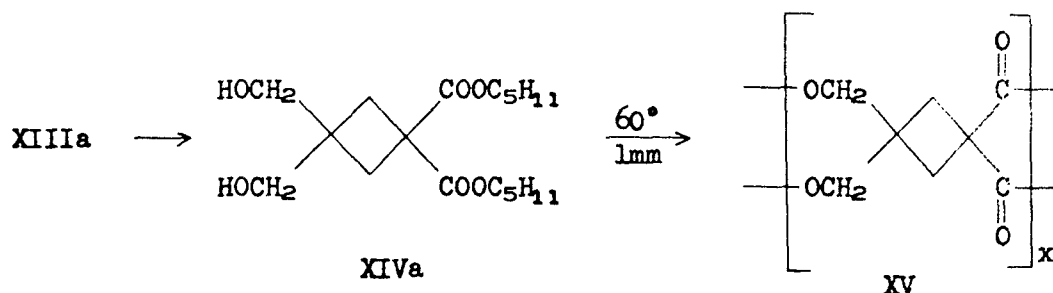
Synthesis of XV from XIVa was accidental and occurred during attempted removal of solvent from XIVa at 60° and a pressure of 1 mm. Subsequent attempts were made to obtain XV from the diethyl ester corresponding to XIVa, diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (XIV), obtained from XIII. Monomer XIV polymerized without a catalyst at 190-200° to evolve water and ethanol. A polymer formed which did not dissolve in any commonly used solvents.

When XIV was heated at 190-200° in the presence of antimony(III) oxide and calcium acetate dihydrate, a polymer formed which was partially dissolved in acetone. No water was evolved when the catalyst was used. Presumably the catalyst prevented formation of ether cross-links which was deduced to have occurred in the uncatalyzed reaction from the fact that water was generated.

Polymer XV has not been characterized as yet.

Another polymer was synthesized from XIII. Treatment of XIII with boron trifluoride etherate in ether gave a polymer which was assigned structure XVI.

$$\text{(diketene/spiro diester)} \xrightarrow{\quad BF_3 \quad} \left[\begin{array}{c} O-CH_2 \quad\quad CH_2 \\ \\ ROOC \quad\quad COOR \end{array} \right]_x$$

COOR

COOR

O

BF₃

O—CH₂   CH₂

ROOC   COOR

XVI

$R = C_2H_5, \; C_5H_{11}$
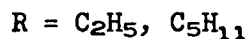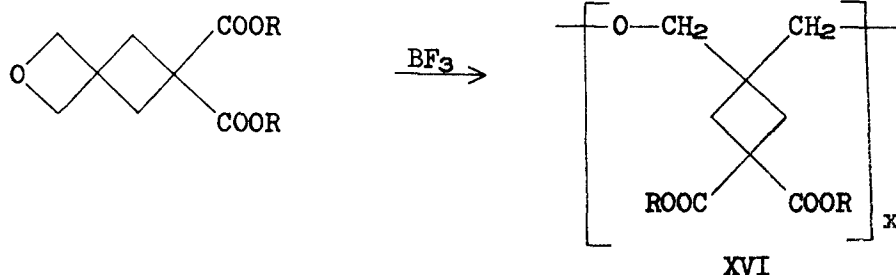
Initially XVI was formed as a clean polymer which remained clear when solvent was removed. If XVI was heated above 80° without complete removal of traces of boron trifluoride etherate, a hard red polymer resulted which was insoluble in all common solvents and was probably extensively cross-linked. If the initially formed polymer was poured into water and washed, it gave a clear white material which was not sensitive to heat and could be dissolved in benzene. Polymer XVI was not characterized further.

Polymer XVI is interesting for investigation as a prepolymer. Conversion of XVI into a spiropolymer offers potential for further study. The possibility exists that some kind of reaction, possibly a trans-esterification, can be found that would convert XVI into a spiropolymer rather than lead to a crosslinked system. However, cross-linked XVI may itself be of some significance.

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SECTION III

FUTURE WORK

Immediate emphasis will be placed on obtaining several grams of
Polymer I using the best presently known conditions. This "best-
possible" Polymer I will be characterized even though it appears the
best material that can be obtained presently contains only eight to
ten repeating monomer units. This same material will be converted into
Polymer II using sulfur tetrafluoride and should give a polymer with
trifluoromethyl end groups. Obtaining a sample of Polymer II for
testing for thermal stability has high priority. For the same reasons
Polymer I will be appropriately reduced to Polymer III.

Although the immediate research emphasis is given in the preceding
paragraph, the overriding emphasis in the next year will be on the
synthesis of high molecular weight Polymer I. Appropriate modifications
of experimental procedures will be attempted.

Even though success in obtaining high molecular weight polymers
seems nearer in the polymerization of XIII and XIV or XIVa, this work
will have secondary emphasis in the near-term research. A minor effort
will be made to synthesize and characterize high molecular weight XV
and XVI.

SECTION IV

EXPERIMENTAL

All temperatures in this report are in degrees centigrade. Melting points were determined in capillary tubes. Infrared spectra were observed with a Perkin-Elmer Infracord Spectrophotometer. Nuclear magnetic resonance spectra were observed with a Varian A-60 Spectrometer. Unless otherwise indicated chemicals were the best grade commercially available for normal chemical synthesis.

A. Synthesis of Dispiro [3.1.3.1.] decane-2,8-dicarboxylic Acid (XII).
Except where otherwise indicated, XII was synthesized by the procedures described in Reference 1.

1. Synthesis of 2,2-Bis(bromomethyl)propane-1,3-diol: From 2720 g. (20.0 mole) of pentaerythritol was obtained 2007 g. (7.68 mole, 38.4%) of 2,2-bis(bromomethyl)propane-1,3-diol, m.p. 108.5-110.0°. Considerable impure product remained in mother liquors which were set aside for later purification when additional dibromide is required.

2. Synthesis of 2-Phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane:
From 2007 g. (7.68 mole) of 2,2-bis(bromomethyl)propane-1,3-diol was obtained 1992 g. (5.69 mole, 74%) of 2-phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane, m.p. 68.0-69.0°. Recovery of additional product from mother liquors was deferred until actually needed.

3. Synthesis of Diisoamyl 7-phenyldioxaspiro[3.5]nonane-2,2-dicarboxylate (VIII): From 927 g. (2.65 mole) of 2-phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane (VII) was prepared 456 g. (1.05 mole, 39.6%) of VIII. During distillation of VIII decomposition was observed. In another run the work-up was modified so that no attempt was made to distill VIII.

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After all lower-boiling material was removed under reduced pressure (to 150° at 0.4 mm) crude VIII was crystallized from methanol. In this way from 736 g. of VII there was obtained 618 g. (1.43 moles, 70.3%) of VIII, m.p. 51.5-52.5°.

The melting point was higher than that reported in Reference 1 which was 44.0-45.0°. The higher m.p. is attributed to better isoamyl alcohol used for the present work. It is fairly certain that the isoamyl alcohol used as a solvent in Reference 1 had other isomeric alcohols present which became part of the ester groups. The infrared and nmr spectra confirm that the material obtained in this work is the same compound as that in Reference 1. However, infrared and nmr absorption bands are sharper for the product reported here indicating higher purity.

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4. **Synthesis of 1,1,3,3,-Tetrakis(hydroxymethyl)cyclobutane(IX):** The preparative procedure was scaled up from that reported in Reference 1 and the work-up extensively modified. From 259.6 g. (0.600 mole) of VIII was prepared 68.8 g. (.390 mole, 65%) of I, an increase in yield of 25% over the work in Reference 1.

The yield increase is directly attributable to a complex work-up procedure which as actually carried out is much too extensive to describe. On the basis of the work in this experiment, a work-up that can be described will be used in the next preparation of IX and reported when appropriate.

---

5. Synthesis of 1,1,3,3-Tetrakis(hydroxymethyl)cyclobutane tetra-p-toluene sulfonate (X): From 68.8 g. (0.390 mole) of 1,1,3,3-tetrakis-(hydroxymethyl)-cyclobutane was prepared 220 g. (0.277 mole, 71.1%) of the corresponding tetrakis-p-toluene sulfonate.

6. Synthesis of Tetraethyl dispiro [3.1.3.1.] decane-2,2,8,8-tetra-
carboxylate: The title tetraester was prepared from 208 g. (0.206 mole)
of diethylmalonate, 25.2 g. (1.10 mole) of sodium, and 183 g. (0.206
mole) of 1,1,3,3-tetrakis-(hydroxymethyl)cyclobutane tetra-p-toluene-
sulfonate in xylene suspension. Work-up gave 92 g. (0.216 mole, 100%)
of crude tetraester whose nmr spectrum indicated that the crude material
was comprised mainly of tetraester.

7. Synthesis of Dispiro[3.1.3.1.]decane-2,2,8,8-tetracarboxylic Acid (XI):
Saponification of 92.0 g. (0.217 mole) of crude tetraethyl dispiro[3.1.3.1]-
decane-2,2,8,8-tetracarboxylic acid gave tetracid XI. Recrystallization
of the crude tetraacid twice from water gave 24.0 g. (0.077 mole, 35.4)
of high-purity (by infrared spectrum) tetraacid XI.

8. Synthesis of Dispiro [3.1.3.1.]decane-2,8-dicarboxylic Acid (XII):
Decarboxylation of 21.0 g. (0.0673 mole) of dispiro[3.1.3.1]-decane-
2,2,8,8-tetracarboxylic acid at 220° under a nitrogen atmosphere gave
12.4 g. (0.0553 mole, 86.3%) of sublimed XII, m.p. 172-175° with sintering
at 168°. For polymerization work XII was recrystallized from water and
resublimed, to give the pure diacid, m.p. 173-175° with sintering at 168°.

B. Poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione) (I) by Polymerization
   of Dispiro[3.1.3.1]decane-2,8-dicarboxylic Acid (XII).

1. Purification of Reagents
   a. Dispiro[3.1.3.1.]decane-2,8-dicarboxylic Acid (XII). The product
      was prepared as described in Part A. For polymerizations the
      diacid was recrystallized from water and resublimed at 160°C. (1 mm).

   b. Triethylamine. Triethylamine (Eastman Catalog No. 616) was heated
      under reflux over finely divided sodium metal for 24 hours. It
      was distilled under nitrogen at atmospheric pressure onto freshly
      cut sodium and stored over sodium under nitrogen.

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c. <u>Thionyl Chloride</u>. Thionyl chloride (Matheson, Coleman and Bell Catalog No. TX-535) was heated for 24 hours under reflux with triphenylphosphite and then distilled at a constant boiling point of 76°C according to the procedure described by Fieser and Fieser (Reference 4).

d. <u>Benzene</u>. Thiophene-free benzene was distilled from sodium and stored over sodium-lead alloy.

2. <u>Poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione) formed in Initial Polymerizations of Dispiro[3.1.3.1]decane-2,8-dicarboxylic Acid</u>. The first attempted polymerization was an obvious failure attributed to insufficiently dried reagents.

In the second polymerization all glassware was flamed for 20 minutes while passing dry nitrogen through the apparatus. Redistilled practical grade thionyl chloride (about 10 ml.) was distilled onto 0.8395 g. (3.75 mmoles) of dispiro[3.1.3.1]decane-2,8-dicarboxylic acid and heated 2 hours at gentle reflux. Excess thionyl chloride was removed under reduced pressure leaving solid pale-white diacid chloride. A mixture of 2 g. of triethylamine in 75 ml. of benzene was distilled from sodium on to the diacid chloride after which the resulting mixture was heated and stirred for 48 hours under reflux.

Insoluble material was filtered from the reaction mixture. When this residue was boiled in hot water insoluble material amounting to 0.050 g., remained, which was designated "High Grade Polymer I". The infrared spectrum of this polymer, shown as Figure 1, is nearly free of any bands assigned as carboxylic acid absorption. The carbonyl peak is shifted from 5.91 microns in the starting material to 5.78 microns in the polymer. A small shoulder on the carbonyl peak suggests carboxylic acid end groups.

"Low Grade Polymer I" was soluble in hot benzene but formed a gel on cooling the solution. The gel was heated with boiling water and benzene,

together with other volatiles, removed by steam distillation. The yield of Low Grade Polymer I after being twice boiled with water and dried amounted to 0.45 g. The infrared spectrum of "Low Grade Polymer I" showed significant carboxylic acid group absorptions (see Figure 2).

No additional characterization of Polymer I was carried out.

3. Poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione) formed by a Standard Procedure for Polymerization of Dispiro[3.1.3.1]decane-2,8-dicarboxylic Acid. To glassware flamed dry under a stream of dry nitrogen, the title diacid (1.00 g., 4.46 mmole) and thionyl chloride (10 ml) were added. Gentle heat was applied by a heating mantle until the diacid dissolved. The 125-ml. reaction vessel was cooled by ice and a vacuum gradually applied to remove thionyl chloride. When no apparent traces of thionyl chloride remained, the reaction flask was warmed to room temperature and kept at a pressure of 0.1 mm for four hours. Nitrogen was admitted and 75 ml. of dry benzene added. Then 10 ml. of dry triethylamine was added and the solution heated until refluxing of the benzene occurred. A white precipitate appeared and after 24 hours white polymer was deposited on the flask walls. The hot mixture was filtered and on cooling the benzene solution formed a gel.

Material on the flask walls was washed with water and dried. This polymer, amounting to 0.10 g., had an infrared spectrum exhibiting a strong 5.78 micron absorption with a weak shoulder about 5.84 microns. No carboxylic acid carbonyl absorption was found at 5.91 microns and the spectrum was almost identical with the spectrum shown in Figure 1. The filtered solid after being washed with water to remove triethylamine hydrochloride amounted to 0.10 g. and had an infrared spectrum nearly identical with material from the walls.

The benzene solution was treated with water and the benzene steam distilled. The product amounted to 0.6 g. and had an infrared spectrum similar to Figure 2. The 5.78 and 5.91 micron carbonyl absorptions were of nearly equal intensity.

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The polymers obtained were not soluble in common solvents after being heated for about one hour under reflux. About 0.2 g. of benzene-soluble polymer dissolved in hexamethylphosphoric triamide.

4. Other Attempts to form Poly(trispiro[3.1.3.1.3.1]tridecane)-1,3-dione by Polymerization of XII. Using procedures similar to those described in Parts B-2 and B-3 above, conditions for polymerization were varied. Only negative results were obtained. Experimental results for several experiments are summarized in Table I.

C. Synthesis and Reactions of Diisoamyl (XIIIa) and Diethyl 6-Oxaspiro[3.3]-heptane-2,2-dicarboxylate (XIII)

1. Synthesis of Diisoamyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate (XIIIa). In a large-scale experiment 173.9 g. (7.60 moles) of sodium were dissolved in 2400 g. (27.2 moles) of constant-boiling isoamyl alcohol, b.p. 131°. Diethyl malonate was added at 70° after which ethanol and isoamyl alcohol were distilled. 3,3-Bis(chloromethyl)oxetane (593.4 g., 3.85 moles) was added dropwise at reflux temperature and the resulting slurry vigorously stirred under gentle reflux for 170 hours.

This product was initially synthesized on a small scale by Mr. Derril Steele in unpublished work that preceded this contract work.

The reaction mixture was cooled and neutralized with 60 ml of acetic acid. Solids were removed by filtration and washed with ether. After ether washings were added to the filtrate and lower-boiling materials removed by distillation at the appropriate reduced pressure, the product distilled at 120-135° (0.01 mm). The product amounted to 415.5 g. (1.27 mole, 33.0%) and was estimated to be 90% pure by comparison of its nmr spectrum with the spectrum of a sample carefully purified by fractionation through a

TABLE I

Attempted Polymerizations to Give Poly(spirocyclobutanes)[1]

Expt.	Reactants[2]	Conditions[2]	Results
1.	0.840 g. (3.75 mmole) dispiro-decane diacid[3] 10 ml. thionyl chloride 75 ml. benzene 2.0 g. (20 mmole) triethylamine	Reflux 48 hours	50 mg. of high-grade polymer whose IR did not show significant C=O due to COOH. Strong 5.78 micron C=O absorption. 45.0 mg. of low-grade polymer with 5.91 and 5.78 micron bands of about equal intensity.
2.	1.00 g. (4.46 mmole) dispiro-decane diacid[3] 10 ml. thionyl chloride 150 ml. benzene 4.0 g. (39 mmole) triethylamine	Reflux 24 hours	108 mg. of high-grade polymer whose IR had a strong 5.78 micron absorption with a very, very weak shoulder. Assumed to be reasonably high molecular weight polymer. 600 mg. of polymer with significant 5.78 micron absorption.
3.[4]	1.00 g. (4.46 mmole) dispiro-decane diacid[3] 10 ml. thionyl chloride 4.0 g. (39 mmole) triethylamine	All thionyl chloride not removed initially. Vigorous reaction over 5-min. period	Red viscous oil which was discarded.

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Table I (Continued)

Expt.	Reactants[2]	Conditions[2]	Results
4.	1.00 g. (4.46 mmole) dispiro-decane diacid[3] 10 ml. thionyl chloride 75 ml. para-xylene 4.0 g. (39 mmole) tripropylamine	Reflux 4 hours	Intractable colored material.
5.	1.00 g. (4.46 mmole) dispiro-decane diacid[3] 10 ml. thionyl chloride 75 ml. toluene 4.0 g. (39 mmole) tripropylamine	Reflux 4 hours	Viscous red oil with very complex infrared spectrum. Intractable material.
6.	1.00 g. (4.46 mmole) dispiro-decane diacid[3] 10 ml. thionyl chloride 75 ml. benzene 4.0 g. (39 mmole) triethylamine	Reflux 72 hours	Hot spots on flask walls gave yellow lower molecular weight (vide infra) polymer. Material not in contact with walls was white and had a clean infrared spectrum corresponding to low-grade polymer (5.91 micron absorption).

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Footnotes

1. Aborted runs not included.
2. Diacid converted to diacid chloride by thionyl chloride. Excess thionyl chloride removed at reduced pressure, solvent added and then trialkylamine added.
3. Dispiro[3.1.3.1]decanedicarboxylic acid.
4. All thionyl chloride not completely removed prior to addition of triethylamine.

spinning-band distillation column. The 10% impurity is deduced to be 1-[2-(diisoamyl malonate)]methyl-1-(chloromethyl)-3-oxetane from the nmr spectrum of a forerun of a spinning-band distillation.

2. **Synthesis of 3,3-Bis(iodomethyl)oxetane.** The method of Campbell (Reference 3) was used to convert 3,3-bis(chloromethyl)oxetane into 3,3-bis(iodomethyl)oxetane in consistent yields of over 90%.

3. **Synthesis of Ethyl tert-butyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate (XIIIb).** Freshly-cut potassium metal (238 g., 6.00 moles) was dissolved in 5 liters of tert-butyl alcohol. Diethyl malonate (480 g., 3.00 moles) was added to the rapidly-stirred potassium tert-butoxide solution over a two-hour period. To the refluxing solution was then added a solution of 3,3-bis(iodomethyl)oxetane (1014 g., 3.00 moles) (Reference 3) and tert-butyl alcohol (800 ml.) over a one-hour period. The solution was stirred and heated under reflux for 48 hours.

The solution was cooled and solids separated by filtration. Water (200 ml.) was added and then removed by azeotropic distillation with benzene. Distillation was continued to remove tert-butyl alcohol. Residual solvent was removed under reduced pressure followed by unreacted diethyl and tert-butyl ethyl malonate. Crude product was collected in the range of 110-130° C. (0.1 mm-Hg) and amounted to 624 g. (78%). The product was identified as tert-butyl ethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate by its nmr spectrum at 60 mcs: singlet at 4.5 ppm, quartet centered at 1.40 ppm (J_{H-H}=8 cps), split singlet at 2.60 ppm, singlet at 1.35 ppm, and a triplet at 1.15 ppm (J_{H-H}=8 cps) downfield from tetramethylsilane. The five absorptions in the spectrum were in the ratio of 4:2:4:9:3 and were assigned, respectively, to oxetane ring -CH_2-, ethyl -CH_2-, cyclobutane -CH_2-, tert-butyl -CH_3 and ethyl -CH_3.

The nmr spectrum also showed that the crude product was contaminated by < 10% 3,3-bis(iodomethyl)oxetane.

The infrared spectrum of the crude product was obtained and the following absorptions in cm^{-1} found to occur with the relative transmittance cited at a baseline of 0.80 relative transmittance: 2850(0.25), 1725(0.05), 1450(0.50), 1410(0.52), 1375(0.45), 1360(0.15), 1275(0.05), 1260(0.07), 1240(0.22), 1180(0.21), 1160(0.15), 1140(0.03), 1070(0.15), 1025(0.55), 980(0.15), 950(0.50), 850(0.40), 740(0.73).

4. Synthesis of Diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate (XIII).
Crude tert-butyl ethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate (50 g., 0.21 mole) was heated under reflux for 24 hours in absolute ethanol (4 liters) to which sodium (1 g.) was added. The resulting solution was cooled and solid carbon dioxide added. The volume was reduced by use of reduced pressure, water was added, and the water-ethanol solution extracted with chloroform. Evaporation of chloroform gave diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate which was distilled at b.p. 112-115° (0.1 mm). The nmr spectrum at 60 mcs had only four absorptions in the ratio 2:2:2:3: singlet at 4.50 ppm, quartet centered at 4.10 ($J_{H-H}=8$ cps) downfield from tetramethylsilane. These absorptions are assigned, respectively, as oxetane $-CH_2-$, ethyl $-CH_2-$, cyclobutane $-CH_2-$, and ethyl $-CH_3$.

The infrared spectrum of the distilled diethyl ester had the following absorptions expressed in cm^{-1} with relative transmittance shown; baseline was at 0.75 transmittance: 2850(0.32), 1725(0.10), 1460(0.45), 1440(0.48), 1410(0.50), 1375(0.50), 1360(0.30), 1275(0.10), 1260(0.10), 1240(0.20), 1180(0.20), 1140(0.10), 1070(0.15), 1025(0.38), 980(0.15), 950(0.40), 850(0.52).

5. Synthesis of Diethyl 3,3-Bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (XIV). Diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate (30.0 g., 0.115 mole) was added to 1.0M sulfuric acid (50 ml) and the mixture heated 10 minutes under gentle reflux. A single phase formed and, after cooling,

the acid was neutralized with solid sodium bicarbonate. The solution was extracted with four 25-ml portions of chloroform. Chloroform was allowed to evaporate and residual traces removed under reduced pressure to give diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate of very high purity as shown by its nmr spectrum at 60 mcs in chloroform solution: quartet centered at 4.60 ppm (J_{H-H}=8 cps), singlet at 4.20 ppm, singlet at 4.0 ppm, singlet at 7.75 ppm, and a triplet centered at 1.60 ppm (J_{H-H}=8.0 cps) downfield from tetramethylsilane.

The infrared spectrum had absorptions in cm^{-1} with relative transmittance (baseline 0.85) as follows: 3300(0.18), 2900(0.30), 1725(0.05), 1475(0.32), 1440(0.35), 1425(0.37), 1380(0.37), 1360(0.20), 1280(0.08), 1260(0.05), 1175(0.12), 1150(0.08), 1100(0.24), 1075(0.24), 1030(0.10), 960(0.68), 900(0.65), 860(0.50).

6. **Synthesis of Diisoamyl 3,3-Bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (XIVa).** By a procedure exactly like that for **XIV**, **XIIIa** had been converted at a much earlier date into **XIVa**. In attempting to remove the last traces of isoamyl alcohol from **XIVa** at 60° and 1-mm pressure, it was observed that a polymer formed.

7. **Polymerization of Diethyl 3,3-Bis(hydroxymethyl)-1,1-dicarboxylate (XIV).** When heated to 200°C under a nitrogen atmosphere, the monomer evolved ethanol and formed a light brown solid polymer which adhered firmly to glass. It required one hour to become solid. Some water was evolved as shown by the nmr spectrum of collected ethanol indicating possible crosslinking by ether linkages. This polymer did not dissolve in any common solvents.

When 5.0 g. of monomer were heated with milligram amounts of antimony(III) oxide and calcium acetate dihydrate under nitrogen at 200°C, it required four hours for a solid to form. An opaque white polymer formed which was partially soluble in refluxing ethyl alcohol and almost

completely soluble in hexamethylphosphoramide. The polymer did not melt when heated to 300°C but turned dark brown.

In another polymerization catalyzed by antimony(III) oxide-calcium acetate dihydrate an acetone-soluble polymer formed.

The polymers were not further characterized.

8. <u>Polymerization of Diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate</u> (**XIII**). When monomer **XIII** was dissolved in diethyl ether at room temperature and an equivalent amount of boron trifluoride etherate was added, no apparent reaction occurred. After 24 hours a small amount of brown solid was present at the bottom of the flask. The ether solution was decanted off and permitted to evaporate. A clear polymer remained which had the consistency of American cheese. No characterization of this polymer was carried out.

REFERENCES

1. C. M. Sharts and A. H. McLeod, *J. Org. Chem.*, 30, 3308 (1965).

2. E. R. Buchman and D. H. Deutsch, Spirane Hydrocarbons, ONR Technical Report, California Institute of Technology (1951).

3. T. W. Campbell, *J. Org. Chem.*, 22, 1029 (1958).

4. L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, John Wiley and Sons, Inc., New York, N. Y. (1967).
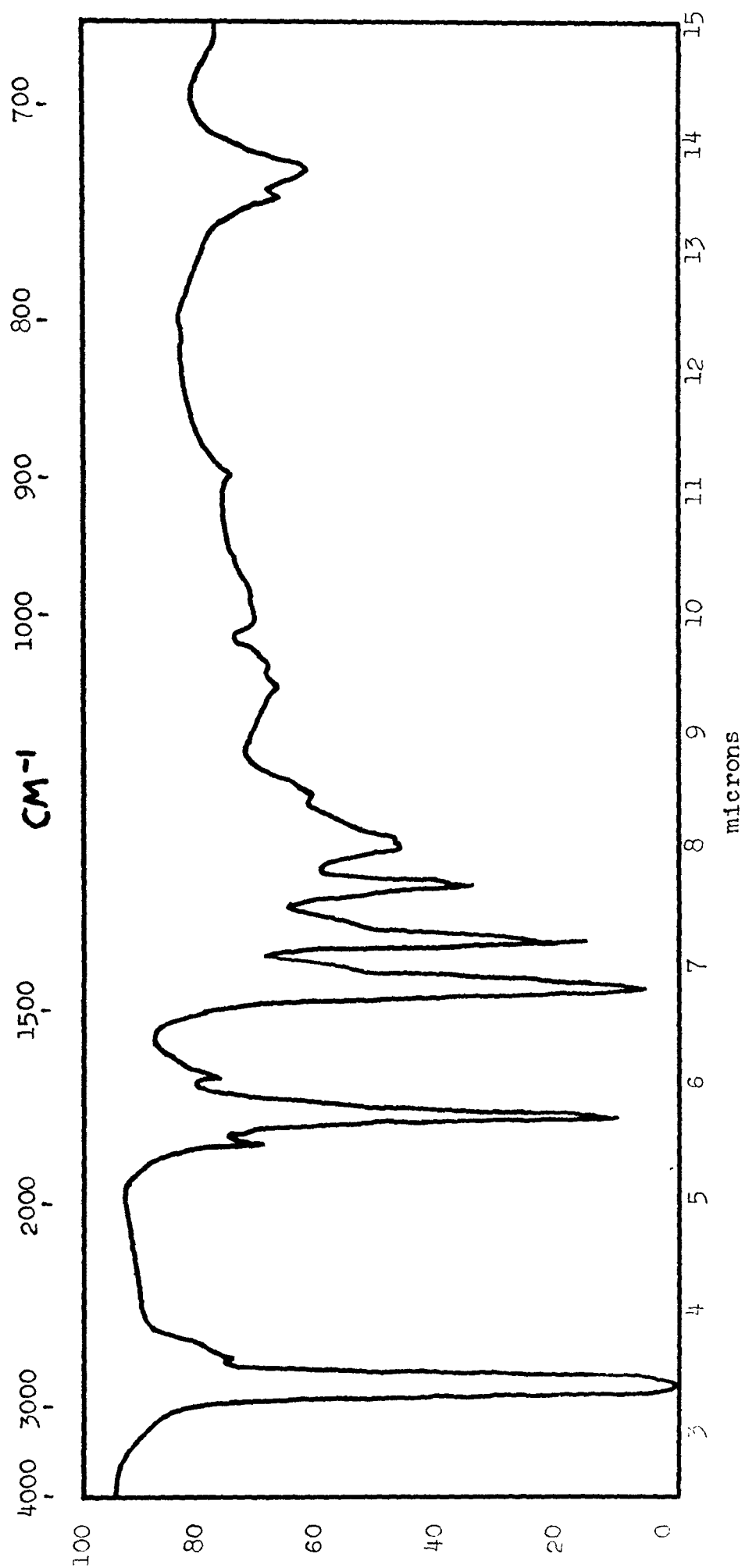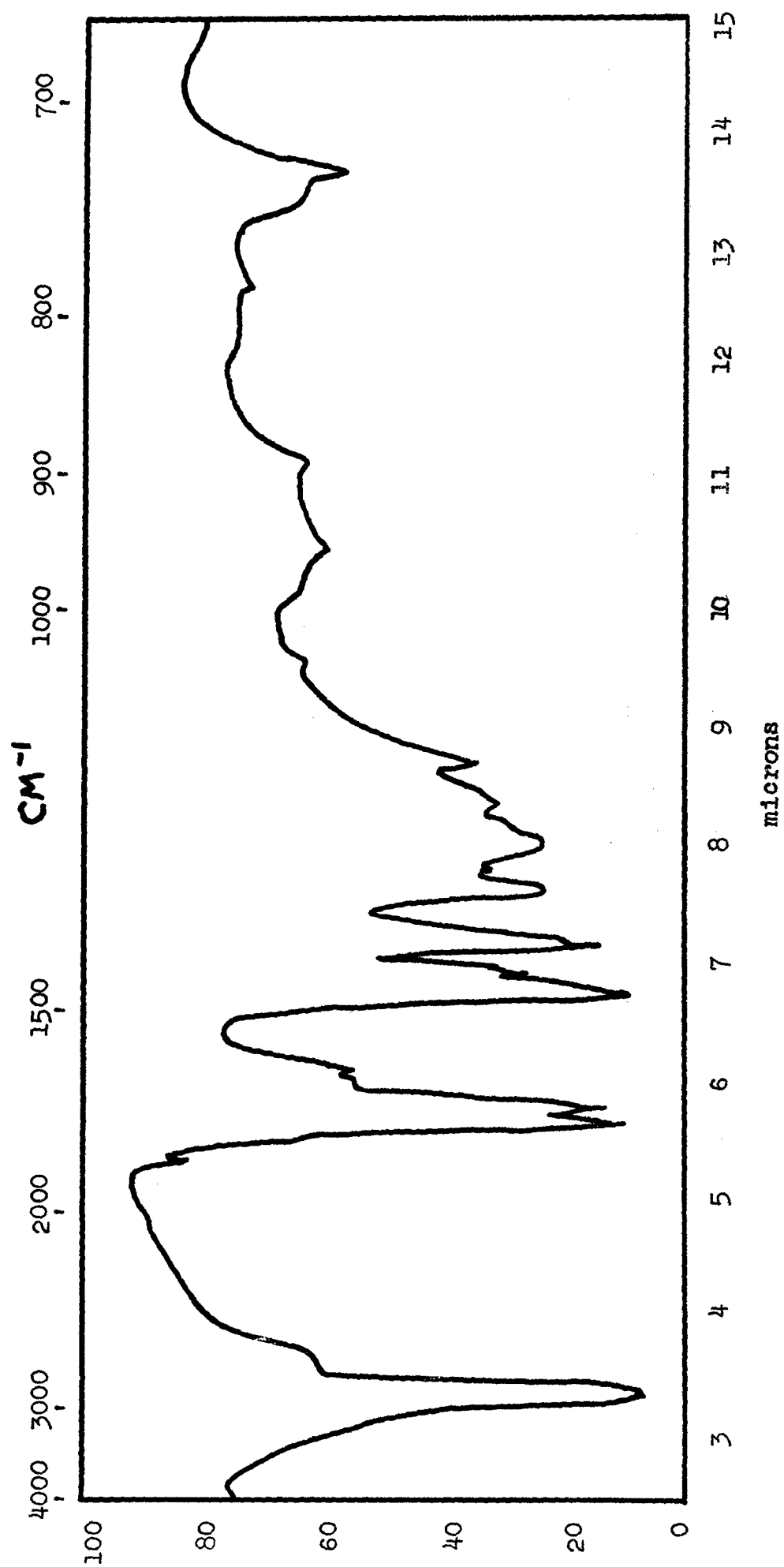
FIGURE 1

Infrared Spectrum of High Grade Polymer I

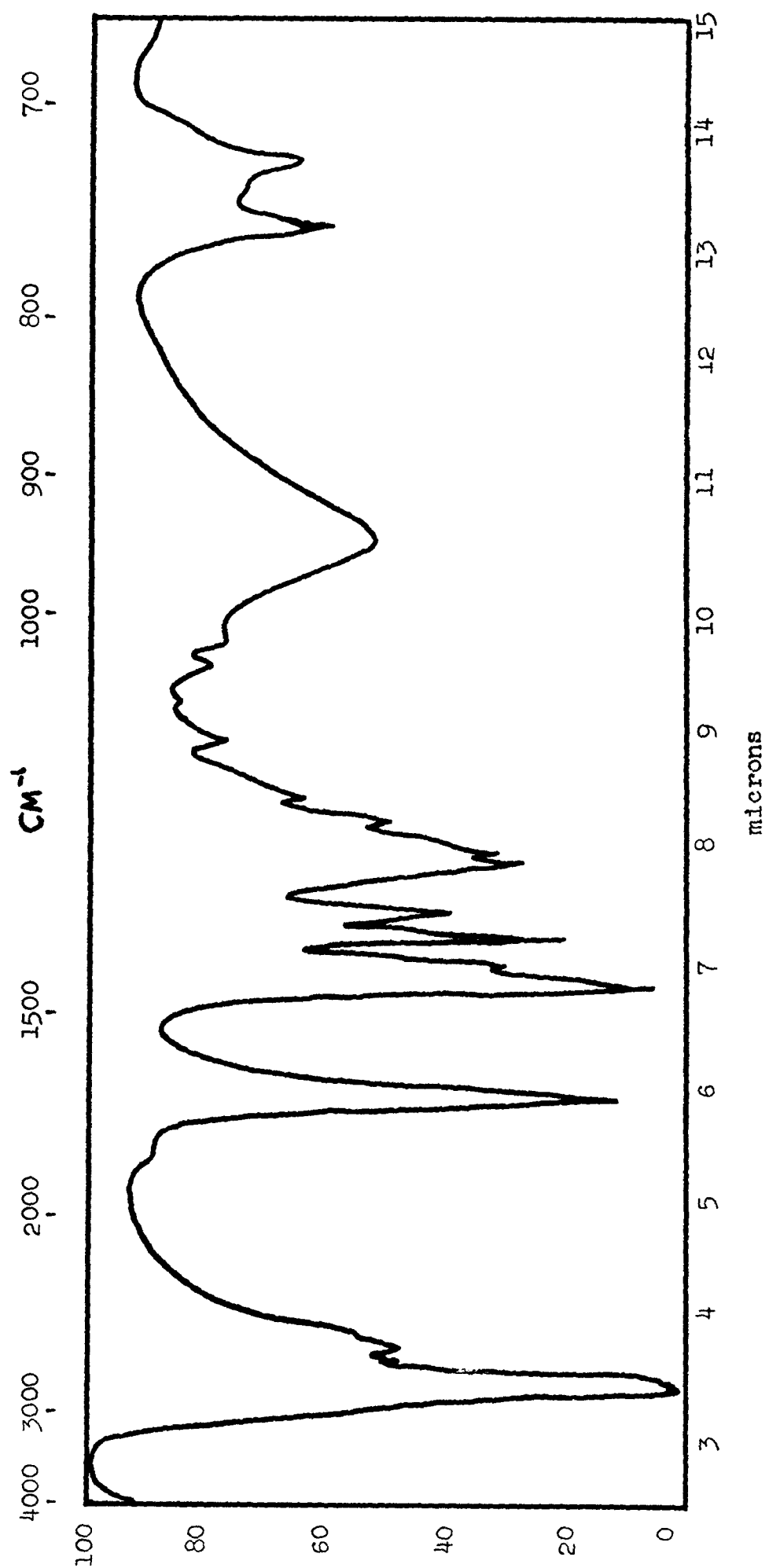FIGURE 2

Infrared Spectrum of Low Grade Polymer I

FIGURE 3

Infrared Spectrum of Dispiro 3.1.3.1 decane-2,8-dicarboxylic Acid

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13. ABSTRACT

Dispiro[3.1.3.1]decane-2,8-dicarboxylic acid was synthesized as a polymer intermediate from pentaerythritol via a seven-step process.

The diacid was converted to dispiro[3.1.3.1]decane-2,8-dicarbonyl dichloride and the bis-acid chloride dehydrohalogenated in benzene solution with triethylamine to give the corresponding diketene derivative. This unisolable monomer polymerized to poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione).

An alternate procedure in place of the tedious synthesis of dispiro[3.1.3.1]-decane-2,8-dicarboxylic acid was investigated. In seeking a short route to the key intermediate, 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane, 3,3-bis(chloromethyl) oxetane was condensed with diethyl malonate to give diisoamyl and diethyl 6-oxaspiro-[3.3]heptane-2,2-dicarboxylate. From these esters were formed diisoamyl and diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate. The hydroxyesters were polymerized to form a spiropolymer whose structure was probably that of poly[3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate].

Boron trifluoride-catalyzed polymerization of diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate gave a polyoxetane.

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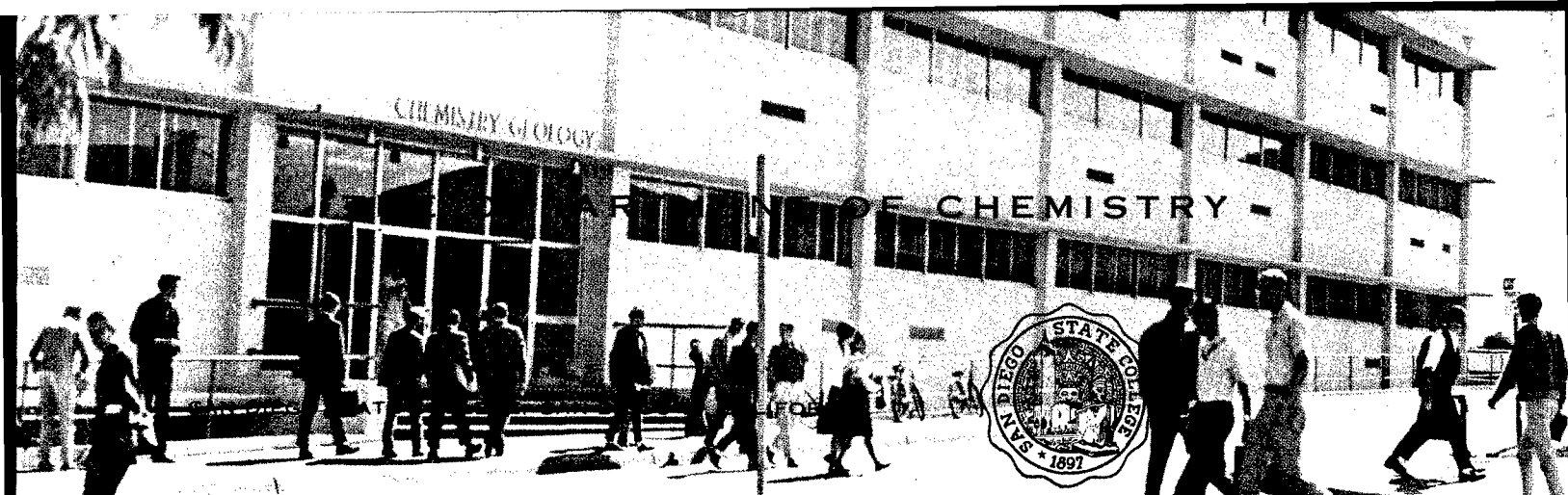| 14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymers						
Spiropolymers						
Spirocyclobutanes						
Pentaerythritol						
Oxetanes						

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A nomenclature error was made consistently throughout
the report.

Change poly(trispiro[3.1.3.1.3.1]tridecane-1,3-dione) to

poly(trispiro[3.1.1.3.1.1]tridecane-1,3-dione)

whereever it occurs in the report. The error occurs on the
cover, title page, in the abstract, table of contents, list
of illustrations and on pages 1, 3, 13, 14, 15, 16, and 27.

Clay M. Sharts